

ROLE OF EXCHANGEABLE CATIONS IN CONCURRENT GASIFICATION/PYROLYSIS OF LIGNITES

Mark E. Morgan* and Robert G. Jenkins

Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

INTRODUCTION

Gasification and combustion of the large reserves of American lignites is an area of intense research. This research, coupled with economic incentives, has led to the current project to build and operate the first large-scale coal gasifier using lignites from North Dakota. However, much work is necessary in order to be able to understand and predict the behavior of these coals. In this paper, the role of ion-exchangeable alkali and alkaline-earth metals in the gasification/pyrolysis of lignites is addressed. These cations, which are peculiar to low-rank coals, are known to have a significant influence on the utilization behavior of lignites. Exchangeable metal cations have been found to affect coal pyrolysis (1,2) and coal-char gasification (3). The goal of this paper is to elucidate the way in which exchangeable cations affect coal gasification in terms of their role in coal pyrolysis, char gasification and the interaction between the two.

EXPERIMENTAL

Pyrolysis was carried out in a dilute-phase entrained-flow reactor. The system is a modified version (4) of that utilized by Scaroni et al. (4). The system allows pyrolysis to be studied under high heating and cooling rates ($10^4 - 10^5$ K/s). Under these conditions, examination of pyrolysis over residence times from 0.03 to 0.30 s and at temperatures up to 1300 K is possible. Pyrolysis occurs in a dilute stream in order to reduce the role of secondary reactions resulting from contact between the pyrolysis products. Because of experimental conditions, weight loss was determined by using ash as a tracer. This technique has been used previously by a number of workers (4,5,6). Weight loss data are reported on a Dry Inorganic Content Free (DICF) basis in order to account for the presence/absence of metal cations.

In this work, four pyrolysis atmospheres were utilized; they are nitrogen, air, carbon dioxide and wet-nitrogen. It should be noted that the volumetric flow rates and gas velocities were the same for all four cases. The wet-nitrogen referred to is saturated nitrogen produced by bubbling dry nitrogen through water at room temperature (2.7% water by volume).

A Montana lignite (Fort Union Seam) was utilized in this study. Details of the organic and inorganic analyses of this coal can be found elsewhere (2). In this study, two types of samples were utilized: raw lignite and acid-washed lignite. In the acid-washing procedure, 50 g of raw lignite, with a mean particle size of 46 μm , were mixed with 900 ml of 0.1 N HCL for 16-24 hours, filtered, and washed repeatedly. It was then refluxed in 1000 ml of boiling distilled water for 1 hour to remove excess HCL (7).

RESULTS AND DISCUSSION

Air and Nitrogen -- The pyrolysis of lignites in air and nitrogen will be discussed first. Combustion in air is treated separately because the highly exothermic oxidation reactions make it difficult to control and predict particle temperature. Thus, the results gained have to be discussed in terms of this experimental difficulty.

* Current Address: Atlantic Research Corporation, Alexandria, VA, 22314.

The results for pyrolysis of the raw and acid-washed lignites in air and nitrogen at 1173 K can be seen in Figure 1. For the sake of clarity, the discussion of these results will be broken into two parts: the effect of the presence of air and the effect of metal cations in air.

In Figure 1, it can be seen that the weight loss behavior is dramatically different in air when compared to nitrogen. While maximum weight loss in nitrogen are 50% for the acid-washed coal and 30% for the raw coal, both coals lose about 90% in air. It should also be noted that major differences between the behavior in nitrogen and air occur at very early residence times. During this initial period, it is assumed that the pyrolysis process dominates the weight loss behavior. Because these increases in weight loss in air occur so rapidly, there are, at least, three proposed mechanisms suggested: oxidation of primary volatiles to reduce secondary char-forming reactions, oxidation of unstable nascent sites in the pyrolyzing char (8), and/or increases in the rate and yield of pyrolysis due to increases in particle temperatures from oxidation reactions.

It can be seen that the presence of metal cations, in air, results in a decrease in the rate of weight loss when compared to the behavior of the acid washed lignite. Figure 1 shows that after approximately 0.05 s the acid-washed lignite has lost 80 wt% whereas the raw lignite has only lost about 30 wt%. It appears that the reason for the observed influence of metal cations is a decrease in the rate of volatile evolution and, thus, oxidation. This view is substantiated by the observation that metal cations have been shown to affect the amount, rate of release and chemical nature of the volatile material (1,2). From Figure 1, it can also be seen that after about 0.15 s the two curves obtained from the runs in air become almost coincident.

Wet-Nitrogen and Carbon Dioxide -- Potentially reactive atmospheres of carbon dioxide and wet-nitrogen were also examined. Analysis of lignite behavior in these atmospheres is somewhat simpler than in air because of the lack of exothermic reactions; especially in any carbon gasification reactions (9).

The results of pyrolyzing the lignite in these two atmospheres can be seen in Figures 2 and 3. In Figure 2, the results for pyrolysis of the raw coal in nitrogen, carbon dioxide and wet-nitrogen are presented. It can be seen that initially weight loss in nitrogen and carbon dioxide are similar but they are greater than in wet-nitrogen. This indicates, probably, a slower heating rate of the particles when wet-nitrogen is the secondary gas. Secondly, it is observed that, at some stage, significant weight loss ceases for all three gases. This leveling off occurs at about 39 wt% in carbon dioxide.

Results for pyrolysis of the acid-washed samples in the three atmospheres are presented in Figure 3. In the case of this sample, similar effects of atmosphere on initial weight loss are observed. That is, initially the weight loss in nitrogen and carbon dioxide are similar and, yet, greater than that observed in wet-nitrogen. However, the most important observation is that there is little, if any, effect of atmosphere on final weight loss in the reactor. After about 0.20 s this acid-washed lignite loses almost 50 wt% in all three gases.

If one compares Figures 2 and 3, an additional interesting result can be found. In all cases, the presence of metal cations in the lignite causes a decrease in total weight loss in the reactor. Although there is a significant increase in weight loss when the raw coal is pyrolyzed in the reactive gases, the largest weight loss for the raw coal is about 40% while the acid-washed sample loses almost 50%. This is in contrast to the weight loss behavior in air where the raw and acid-washed samples have similar weight loss values after about 0.15 s.

As stated previously, during pyrolysis in wet-nitrogen or carbon dioxide, it is possible to eliminate large differences in particle time-temperature history as a source of differences in gasification behavior. Therefore, the two major causes of the observed behavior in these atmospheres are related to reactions of the atmospheres with the pyrolyzing solid surface and/or reactions with the volatile materials released. Of these two explanations, it appears that the second is more likely to be dominant. This suggestion arises from two observations. Firstly, the increases in weight loss occur most dramatically during the initial 0.15 s when the release of volatile species should dominate the coal's behavior. Secondly, these gases appear to have little influence on the ultimate pyrolysis behavior of the acid-washed lignite. It has been shown that the presence/absence of metal cations in lignites profoundly affects the evolution of volatile species at short residence times. Thus, removal of the metal cations enhances volatile yield to such a degree that the presence of the various gases has little or no effect on the observed behavior.

ACKNOWLEDGEMENTS

This study was performed with support from USDOE under Contract No. DE-AC01-79ET14882. We wish to thank Professor W. Spackman for supplying the coal from the Penn State Coal Sample Bank, Coal Research Section, The Pennsylvania State University.

REFERENCES

1. Morgan, M. E. and Jenkins, R. G., A.C.S. Fuel Chemistry Preprints, 1983, (28), 4, 138.
2. Morgan, M. E., Ph.D. Thesis, The Pennsylvania State University, University Park, PA, 1983.
3. Walker, P. L., Jr., Matsumoto, S., Hanzawa, T., Miura, T. and Ismail, J. M. K., Fuel, (62), 1983, 140.
4. Scaroni, A. W., Walker, P. L., Jr. and Essenhigh, R. H., Fuel, 1981, (60), 71.
5. Anthony, D. B. and Howard, J. B., AIChE Journal, 1976, (22), 625.
6. Badzioch, S. and Hawksley, P. G. W., Ind. Eng. Chem. Process Des. Dev., 1970, (9), 521.
7. De, G. S., Tumuluri, S. and Lahari, K. C., Fuel, 1971, (50), 272.
8. Johnson, J. L., Kinetics of Coal Gasification, John Wiley and Sons, Inc., NY, 1979.
9. Walker, P. L., Jr., Rusinko, F. and Austin, L. G., Adv. in Cat., 1959, (11), 133.

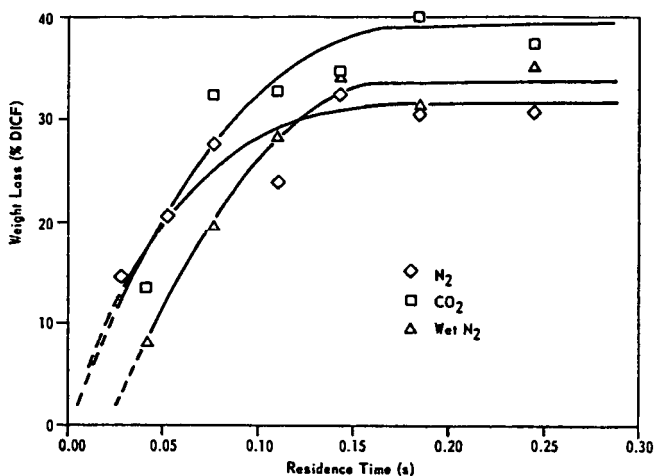


Figure 2. WEIGHT LOSS IN ENTRAINED FLOW REACTOR
IN N_2 , CO_2 AND WET N_2
Raw Montana Lignite, 270 x 400 Mesh

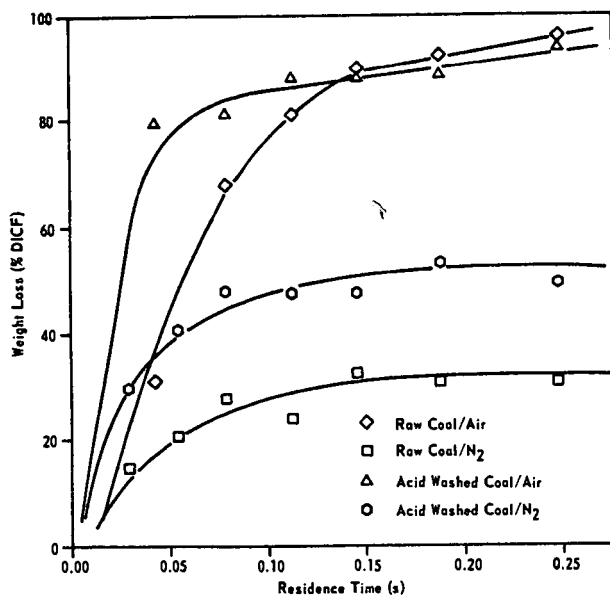


Figure 1. WEIGHT LOSS IN ENTRAINED FLOW REACTOR
IN AIR, 1173K

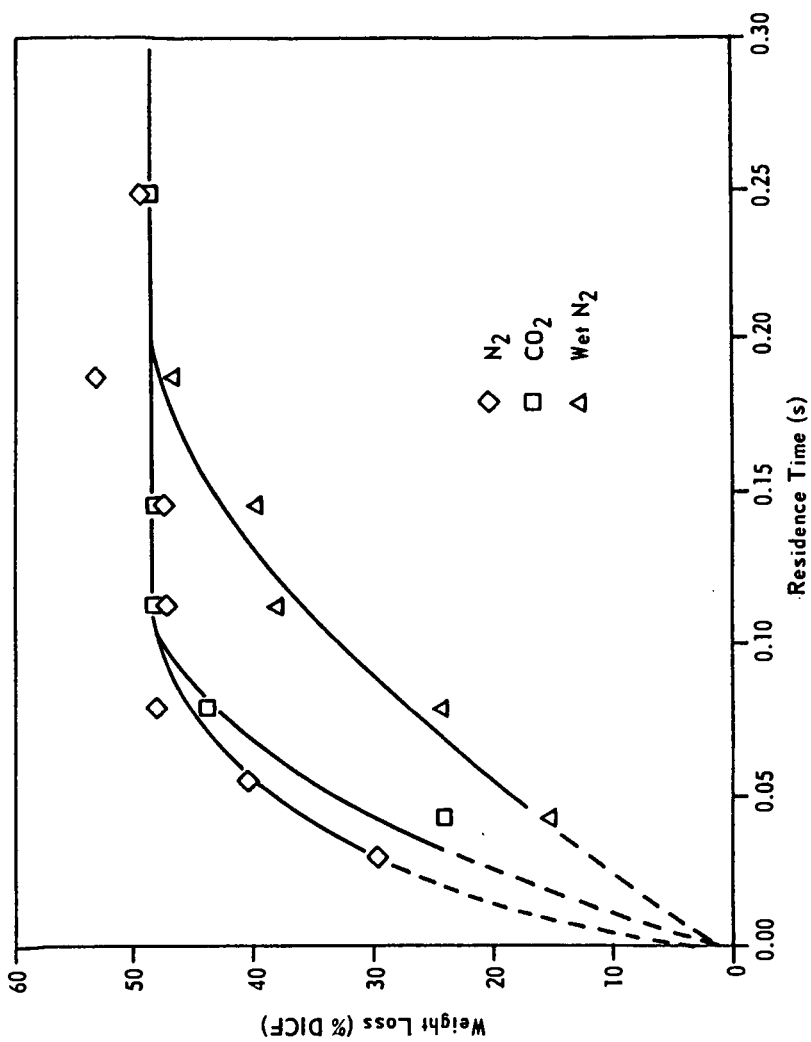


Figure 3. WEIGHT LOSS IN ENTRAINED FLOW REACTOR
IN N_2 , CO_2 AND WET N_2
Acid Washed Montana Lignite, 270 x 400 Mesh